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Trapping Hydrogen in Ice

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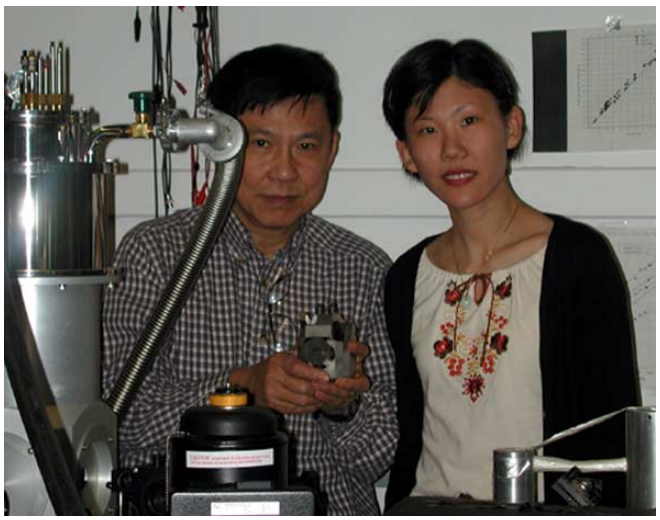
Until recently, scientists thought that molecular hydrogen was too small to be contained in clathrate hydrates—crystalline solids made of a crystalline lattice of water molecules enclosing molecules of another substance, usually a noble gas. Using x-rays produced at beamline X17B of the National Synchrotron Light Source at Brookhaven National Lab. in Upton, NY, scientists from the Univ. of Chicago and the Carnegie Institution of Washington have reported the formation of a hydrogen clathrate hydrate – in which hydrogen molecules are completely enclosed in a lattice of water molecules – that is quenchable to ambient pressure at temperatures below 110 Kelvin. This material may have implications for research in hydrogen fuel storage, superfluidity, and astrophysics.

Hydrogen molecules are considered to be too small to be enclosed in one of four possible structures of clathrate hydrates, compounds in which molecules of a substance are completely enclosed within the crystal structure of water. The three clathrate structures that do not to include hydrogen molecules are denoted sI, sII, and sH. Instead, hydrogen molecules have been found to fill small cavities in ice II and ice Ic at high pressures.

We have synthesized a hydrogen hydrate with the classical sII structure (HH-sII) and a high hydrogen:water ratio (= 0.45 ± 0.05). This high ratio shows that, unlike most clathrate hydrates, where only one molecule of a gas can be trapped inside the clathrate cage, many hydrogen molecules are entrapped in two types of cages (a small and a large one) within each clathrate compound. Two hydrogen molecules are enclosed in the small cages and four in the large cages (**figure 1**).

HH-sII is stable or metastable – unstable in the absence of certain conditions that would induce stability – to ambient pressure and low temperature after initial synthesis at moderate pressure. We compressed a mixture of hydrogen and water to 180–220 megapascals (about 2,000 times the atmospheric pressure) at 300 Kelvin –in a diamond anvil cell, which separated the samples into two regions: a hydrogen bubble and liquid water. We noticed that, upon cooling to 249 Kelvin, the two fluids reacted and formed a single, solid compound.



Authors Ho-kwang Mao (holding the diamond anvil cell) and Wendy L. Mao standing beside the cryostat used in the experiments conducted at NSLS beamline X17B.

Using energy dispersive x-ray diffraction (EDXD) at beam line X17B of the National Synchrotron Light Source at Brookhaven National Laboratory in Upton, New York, we observed 21 diffraction peaks at 220±30 megapascals and 234 Kelvin (**figure 2**). The EDXD pattern reveals that the formed clathrate contains a face centered cubic (fcc) unit cell with a = 17.047 ± 0.010 angstrom, in excellent agreement with the sII clathrate. We attribute two hydrogen molecules to each pentagonal dodecahedron cage (structure with 12 pentagon faces) and four hydrogen molecules to each hexakaidodecahedron cage (structure with four hexagon faces and 12 pentagon faces).

Once HH-sII was synthesized at 200 megapascals, it showed remarkable stability or metastability and persisted to 280 Kelvin upon warming. The clathrate was also cooled to 78

Kelvin, and then pressure was released completely. This sample was then exposed to vacuum in the cryostat, and the clathrate remained (did not decompose). The large hydrogen storage capacity and stability of HH-sII at ambient pressure make it a potential hydrogen fuel storage material.

Since HH-sII can be synthesized at a pressure of more than 180 megapascals, which is within the range of interior conditions of small, icy satellites, this clathrate could hold hydrogen to high temperatures in bodies which were previously thought to be incapable of retaining hydrogen.

The kinetics of possible *in-situ* formation of HH-sII at low-pressure interstellar conditions has not yet been explored. But this clathrate could be grown epitaxially (growth upon the surface of another crystal) on substrates of other sII clathrates or by annealing (heating to remove or prevent internal stress) hydrogen in amorphous ice. The intriguing physics and chemistry of filling large cages with clusters of small molecules also opens new directions in clathrate and ice research.

Confining hydrogen molecular clusters in cages also provides a new means for studying novel interactions and quantum effects, such as the proposed superfluidity and Bose-Einstein condensation of hydrogen molecular clusters.

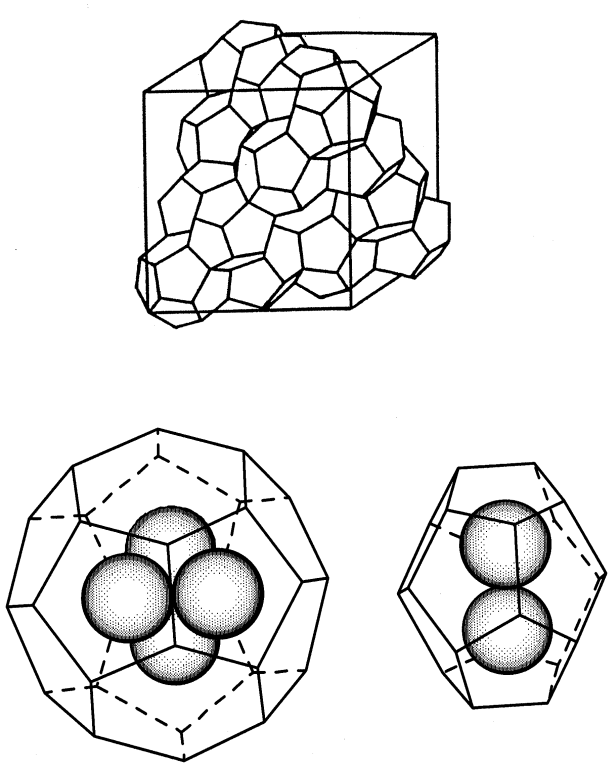


Figure 1. *(Top) sII crystal structure consisting of large and small cages. (Bottom left) A tetrahedral cluster of four hydrogen molecules in a large cage. (Bottom right) A cluster of two hydrogen molecules in a small cage.*

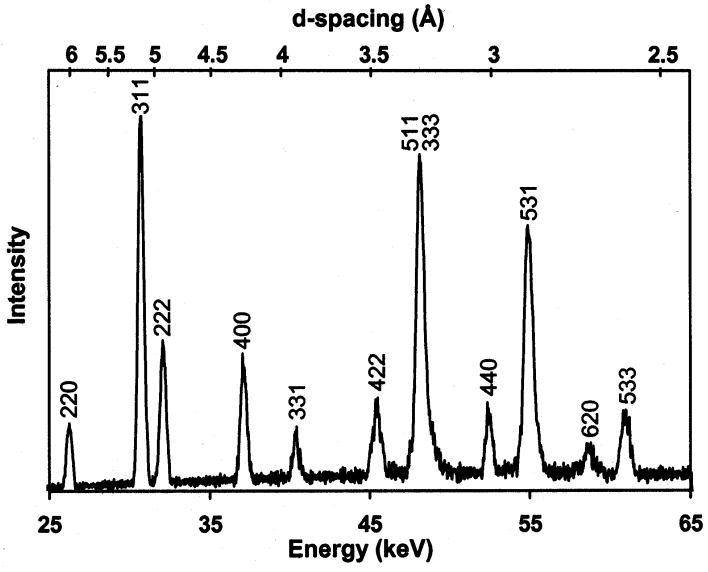


Figure 2. *Energy dispersive x-ray diffraction pattern of HH-sII at 220 megapascals and 234 Kelvin (2q = 4.50 degrees). The Miller indices,* h, k, *and* l *are marked on each peak.*